A New Mode of Interaction of Carboxylic Acids with Some N-phenylbenzohydroxamates of Copper(II), Cobalt(II) & Nickel(II)

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A new type of interaction of acetic acid, halogeno substituted acetic acids and benzoic acid with some N-phenylbenzohydroxamates of copper(II), cobalt(II) and nickel(II) has been demonstrated from the spectral studies. In this type of reaction, the carboxylic acids behave as Lewis bases. Bis-adducts of general formula $M(LL)_2(HA)_2$, where $M = Cu(II)$, Co(II), Ni(II); LL = anion of hydroxamic acids; and HA = aliphatic carboxylic acids, have been isolated. These six-coordinated complexes have been characterized; these are stabilized by strong intra- and/or inter-molecular hydrogen bonding.

The reactions of protic materials with transition metal chelates have significance in relation to biological systems. Interaction of added protic materials with metal chelates may result in partial removal of one or more chelating ligands via some intermediate species[1,2]. Examples of this type are the reactions of some haloacetic acids with copper(II) complexes of oxine and salicylaldehyde which have been described recently[1,2]. Another situation may arise when the chelate rings in the original complex on reaction with the acidic substances, are opened up to act as monodentate ligands but are not dissociated completely from the metal centre[3-5]. Simultaneous coordination of carboxylic acid oxygen to the metal and its hydrogen bonding with a coordinated atom of a ligand are unknown. The present paper, therefore, describes the latter type of interactions of a number of carboxylic acids with some N-phenylbenzohydroxamates of copper(II), cobalt(II) and nickel(II).

Materials and Methods

Preparation of hydroxamates of Cu(II), Ni(II) and Co(II)—The metal chelates with the ligands N-o-tolylbenzohydroxamic acid (ligand A), N-o-tolyl-o-toluohydroxamic acid (ligand B), N-phenyl-o-toluohydroxamic acid (ligand C) and N-phenylbenzohydroxamic acid (ligand D) used in this study have been prepared as reported earlier[6-9].

The carboxylic acids, acetic acid, and monochloro-, dichloro-, trichloro- and trifluoro-acetic acids were purified by fractional distillation. Benzoic acid (AR) was recrystallized from ethanol-water.

1,2-Dichloroethane (DCE) was purified and dried. Benzene (GR, E. Merck) was dried over metallic sodium and then distilled; the middle fraction was used for cryoscopic measurements and recording of absorption spectra. Pure acetonitrile was fractionally distilled over calcium hydride.

Spectral studies: (a) *Cu(II) complexes*—Stock solutions of the complexes were prepared separately by dissolving the complexes in dry DCE by warming, if necessary. Aliquots of the stock solutions were transferred to a number of volumetric flasks to which different amounts of each of the carboxylic acids in DCE were added. The volume was made up to the mark in each case and the spectrum of each solution was recorded at an interval of 10 nm in the range 450-900 nm with the help of a Hitachi 200 spectrophotometer. In the case of acetic acid, however, varying amounts of the acid were directly weighed in stoppered volumetric flasks and fixed aliquots of the hydroxamates in DCE were added. The volume was made up to the mark in each case and then the spectrum obtained as described earlier.

(b) *Ni(II) and Co(II) complexes*—A known quantity of a cobalt or nickel chelate was suspended in about 5 ml of dry and purified benzene and to it different amounts of carboxylic acids in benzene were added separately. The mixtures were diluted to 10 ml with benzene so that the final concentration of the complex was $0.05\ M$ with respect to the metal ion. The spectra of the solutions were then recorded at an interval of 10 nm in the range 450-1300 nm for solutions containing nickel(II) complexes and 630-1300 nm for solutions containing cobalt(II) complexes. In the case of cobalt(II) complexes, the original solutions were diluted 5 times to obtain the absorption spectra in the higher energy region (450-630 nm). The initial amount of the acid used was such as to give a final concentration of $0.1\ M$ when diluted to 10 ml. The concentrations of the acids were then increased slowly till the absorption spectrum of the resultant mixture did not change with the further increase in the concentration of the acid.

Isolation of the carboxylic acid adducts of Cu(II), Ni(II) and Co(II)—Complexes of Cu(II), Ni(II) and

Co(II) (1.25 mmol) were separately suspended in about 15 ml of benzene followed by the addition with constant stirring of a solution of trifluoro-, trichloro- or dichloro-acetic acid (3.1 mmol) in about 5 ml of benzene. The colours of the resulting solutions changed appreciably on adding the acids. The solutions were then filtered, diluted with ligroin (40°-60°) and kept at room temperature or in the cold till crystallization was almost complete. The separated crystals were filtered, washed with benzene-ligroin mixture (1:4) and dried *in vacuo*. In the case of $Cu(D_2)$-trichloroacetic acid adduct, the green coloured solution was kept in a refrigerator overnight when green crystals along with an oily mass were obtained; the latter was removed by washing with benzene. In the case of monochloroacetic acid, the amount of acid used was 6-8 mmol and with acetic acid, the quantity of acid added was about 100 mmol. In the latter two cases, however, no compound could be isolated.

Magnetic susceptibilities of the complexes were determined using a Gouy balance. Cryoscopic measurements in dry benzene were carried out using a Beckmann differential thermometer, calibrated to 0.01°. A Philips PR 9500 conductivity bridge was employed for conductance measurements of solutions (0.001 M) of complexes in dry acetonitrile. The visible absorption spectra of the complexes were obtained in dry benzene with Hitachi 200 or Spectromom 204 spectrophotometer. The infra red spectra of the complexes were recorded in nujol as well as in KBr on a Perkin Elmer 297 IR spectrophotometer.

Results and Discussion

The spectra obtained by the interaction of one of the hydroxamates, $Cu(A)_2$, with acetic acid in DCE in the presence of varying amounts of acetic acid are shown in Figs 1a and 1b. In Fig. 1a, curve 1 represents the spectrum of 0.01 M solution of $Cu(A)_2$ in pure DCE. Other curves in Fig. 1a were obtained with a fixed concentration of copper complex and a progressively increasing amount of acetic acid up to a molar ratio (MR) of 25.4:1 of the acid: copper complex. These curves show that with an increase in the [acid], the absorption maximum at 600 nm gradually shifts towards higher wavelengths (620-30 nm) with a simultaneous increase in its intensity. The shoulder at 770 nm slowly but eventually disappears. The single isosbestic point observed at 570 nm in this concentration range of the acid suggests a one step equilibrium involving the original species and probably a mono-adduct. In Fig. 1b, curves 4-8 were obtained by a further increase in the acid concentration up to MR of 350. Thus, a further increase in the acid concentration produces a second isosbestic point at 596 nm confirming another
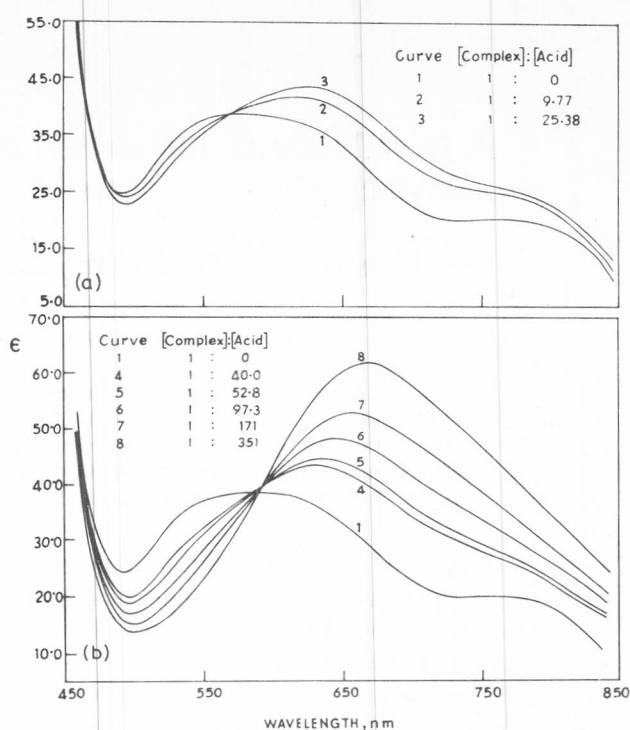

Fig. 1—Spectra of DCE solutions of CuA_2 containing varying amounts of acetic acid

equilibrium presumably between the mono-adduct and the final bis-adduct, the absorption maximum of which is observed at 670 nm. In the case of the mono-adduct, a limiting absorption was never attained; instead, the second step of the reaction i.e. formation of the bis-adducts took place with the increase in acid concentration. In the case of bis-adducts also, even a 350-fold excess of the acid did not produce completely the final product. However, with the further increase in [acid], the compound is probably decomposed since the absorption curve no longer passes through the isosbestic point at 596 nm and the absorption enhances sharply with a change in absorption maximum. Similar studies were carried out using $Cu(B)_2$ and $Cu(C)_2$ complexes and also using other carboxylic acids. The two isosbestic points, the concentration ranges of the acid at which they were achieved and the positions of the absorption maximum for the final products are given in Table 1.

The changes in the colours of the complexes and the changed spectral behaviour are the most important features of the reaction of the carboxylic acids with bis(hydroxamato) complexes of nickel(II) and cobalt(II). The absorption maxima and the corresponding molar extinction coefficients of the nickel(II) and cobalt(II) hydroxamates in benzene containing carboxylic acids, are given in Table 2.

The cobalt(II) hydroxamates are dimeric and five-coordinated[6,7] having absorption maxima around 750

Table 1—Spectral Data on the Interaction of Carboxylic Acids with Copper(II) Hydroxamates

Acid	Complex	First isosbestic point (nm)	M:R range for first isosbestic point	Second isosbestic point (nm)	M:R range for second isosbestic point	ε_{max} for Bis-adducts	λ_{max} for the final product (nm)
	CuA$_2$	570	0-25.4	596	40-351	‡	670
Acetic	CuB$_2$	582	0-38.0	592	38-233	‡	670
	CuC$_2$	596	0-32.8	600	45.9-175	‡	670
	CuA$_2$	584	0-1.0	602	3-8.0	42.4	640
Monochloroacetic	CuB$_2$	590	0-1.0	606	3-6.0	47.5	650
	CuC$_2$	†	—	606	1-4.0	43.7	650
	CuA$_2$	†	—	618	1-2.5	42.8	660
Dichloroacetic	CuB$_2$	†	—	600	1-3.5	43.2	670
	CuC$_2$	†	—	608	0.5-3.5	46.0	680
	CuA$_2$	600	0-1.0	618	1-3.0	48.6	700
Trichloroacetic	CuB$_2$	†	—	612	1-2.5	48.9	690-700
	CuC$_2$	596	0-1.5	610	1.5-3.0	53.5	710
	CuA$_2$	610	0-0.75	624	1.0-3.0	47.5	700
Trifluoroacetic	CuB$_2$	†	—	622	1.0-2.5	47.5	710
	CuC$_2$	†	—	620	1.0-3.0	49.0	700

†not clear; ‡could not be observed.

Table 2—Absorption Maxima (nm) and Molar Extinction Coefficients of Nickel(II) and Cobalt(II) Hydroxamates in Benzene Containing Carboxylic Acids

Metal hydroxamate	λ_{max} in presence of					
	CH$_3$COOH‡	CH$_2$ClCOOH	CHCl$_2$COOH	CCl$_3$COOH	CF$_3$COOH	C$_6$H$_5$COOH
	630	630	630	†	620	620
	(8.16)	(6.94)	(7.14)		(8.40)	(9.14)
NiA$_2$	1030	1030	1030		1020	1020
	(8.44)	(7.20)	(8.24)		(11.16)	(9.44)
	1100	1100	1110		1100	1110
	(sh)	(sh)	(sh)		(sh)	(sh)
	630	630	630	630	630	630
	(7.18)	(6.90)	(7.24)	(8.84)	(6.24)	(8.14)
NiB$_2$	1030	1030	1030	1030	1030	1020
	(8.16)	(7.52)	(7.50)	(7.30)	(9.80)	(9.28)
	1110	1100	1100	1090	1100	1110
	(sh)	(sh)	(sh)	(sh)	(sh)	(sh)
	620	620	620	630	630	630
	(7.10)	(8.34)	(7.98)	(7.10)	(6.72)	(8.70)
NiC$_2$	1040	1020	1020	1030	1030	1030
	(8.10)	(8.10)	(7.18)	(7.56)	(8.32)	(9.84)
	1100	1100	1115	1110	1110	1110
	(sh)	(sh)	(sh)	(sh)	(sh)	(sh)
	500	500	500	510	510	500
	(32.10)	(36.70)	(36.60)	(64.90)	(42.50)	(50.70)
CoA$_2$	1040	1040	1040	1040	1050	1050
	(3.46)	(3.36)	(3.58)	(4.98)	(5.60)	(6.64)
	1090	1090	1090	1090	1100	1100
	(2.94)	(3.25)	(3.14)	(5.10)	(5.30)	(6.12)
	500	500	500	510	520	510
	(37.60)	(25.60)	(40.50)	(67.20)	(41.50)	(33.30)
CoB$_2$	1040	1040	1040	1040	1050	1050
	(2.70)	(3.52)	(5.72)	(5.64)	(3.12)	(4.24)
	1090	1090	1090	1090	1100	1100
	(2.60)	(3.48)	(5.36)	(6.00)	(2.90)	(3.88)
	510	510	510	510	490	500
	(43.80)	(21.00)	(27.90)	(41.20)	(86.00)	(55.50)
CoC$_2$	1040	1040	1040	1040	1050	1050
	(5.66)	(3.14)	(3.70)	(3.06)	(7.30)	(5.54)
	1090	1090	1090	1090	1100	1100
	(5.16)	(3.06)	(3.54)	(3.12)	(6.66)	(5.28)

†the adduct is precipitated.   ‡ε values are given in parentheses.

nm and 550 nm in benzene, there being no other absorption maximum near 1000 nm. On adding an acid to a cobalt hydroxamate in benzene, the maximum around 750 nm disappears but a new absorption maximum is observed above 1000 nm. Moreover, the spectral curve in the low energy region is composed of two closely spaced absorption maxima near 1040 and 1090 nm. The highest energy band is slightly shifted towards lower wavelengths (490-520 nm, Table 2).

The nickel(II) hydroxamates are trimeric and octahedral[6,8] having three absorption maxima at 655-665, 770-810 (shoulder) and 1010-1030 nm with molar extinction coefficient values in the range 6.20-8.20. In presence of an acid, the highest energy band shifts to

620-630 nm whereas the lowest energy band undergoes a slight red shift (from 1010-30 nm to 1020-40 nm). The shoulder that is observed near 800 nm in the original hydroxamates is absent in the adducts.

The spectral changes mentioned above could be due to (i) partial removal of hydroxamic acid, (ii) opening up of the chelate ring so that the hydroxamic acid acts as a monodentate ligand, or (iii) addition of acid molecules. In order to find out the mode of interaction of these protic materials with the metal hydroxamates, attempts have been made to isolate the addition products in all the cases. However, only twenty adducts could be isolated (Table 3) in the solid state though in solution it has been shown that such adducts exist in all the cases. All the aducts, except with benzoic

Table 3—Characterisation Data on Carboxylic Acid Adducts

Complex	Colour (m.p., °C)	Found (Calc.), %		μ_{eff} (B.M.)	Λ (mho mol^{-1} cm^2)	Molec. Wt. Found (Calc.)
		Metal	N			
$CuA_2(CCl_3COOH)_2$	Green (92-96)	7.55 (7.53)	3.53 (3.32)	1.95	2.1	724 (844)
$CuB_2(CCl_3COOH)_2$	Bluish green (132-136)	7.17 (7.30)	3.47 (3.22)	1.72	1.5	773 (871)
$CuC_2(CCl_3COOH)_2$	Yellowish green (94-100)	7.60 (7.53)	3.04 (3.32)	2.07	2.7	815 (844)
$CuD_2(CCl_3COOH)_2$	Green (124-128)	7.85 (7.80)	3.64 (3.44)	1.80	1.4	701 (815)
$CuA_2(HCCl_2COOH)_2$	Green (94-96)	8.59 (8.53)	3.62 (3.48)	1.95	13.6	732 (775)
$CuA_2(CF_3COOH)_2$	Green (112-120)	8.39 (8.20)	3.54 (3.76)	1.87	45.0	740 (745)
$NiA_2(CHCl_2COOH)_2$	Light green (172)	7.71 (7.64)	3.28 (3.64)	3.25	42.6	—
$NiA_2(CCl_3COOH)_2$	Green (173)	6.89 (7.01)	3.44 (3.34)	3.21	0.2	—
$NiA_2(CF_3COOH)_2$	Grass green (165)	8.16 (7.95)	3.72 (3.79)	3.21	54.6	—
$NiB_2(CCl_3COOH)_2$	Green (180)	6.79 (6.78)	3.22 (3.23)	3.30	0.2	809 (866)
$NiC_2(CCl_3COOH)_2$	Light green (185)	6.92 (7.01)	3.37 (3.34)	3.21	0.3	—
$NiC_2(C_6H_5COOH)$	Grass green (209)	9.25 (9.28)	4.36 (4.43)	3.33	6.4	971 (633)
$CoA_2(CHCl_2COOH)_2$	Chocolate (153)	7.91 (7.67)	3.31 (3.64)	4.94	26.8	627 (769)
$CoA_2(CCl_3COOH)_2$	Light pink (150)	7.40 (7.04)	3.59 (3.34)	4.95	0.3	—
$CoA_2(CF_3COOH)_2$	Pink (178)	8.17 (7.98)	3.83 (3.79)	5.27	56.3	—
$CoA_2(C_6H_5COOH)$	Violet (132)	9.40 (9.32)	4.32 (4.42)	4.91	3.5	—
$CoB_2(CHCl_2COOH)_2$	Pink (130)	7.74 (7.40)	3.51 (3.52)	4.91	21.1	899 (797)
$CoB_2(CCl_3COOH)_2$	Pink (148)	6.83 (6.81)	3.39 (3.23)	4.75	0	1008 (866)
$CoB_2(CF_3COOH)_2$	Violet (174)	7.74 (7.69)	3.68 (3.65)	5.08	48.6	1118 (767)
$CoC_2(CCl_3COOH)_2$	Pink (168)	7.37 (7.04)	3.33 (3.34)	4.91	0.2	999 (838)

Table 4—IR Data (cm^{-1}) of the Acid Adducts of the Cu(II), Co(II) and Ni(II) Hydroxamates

| Complex | Hydroxamic acid $\nu C = O$ | Carboxylic acid | | | |
		νOH	$\nu_{as} COO$	$\nu_s COO$	δ_{O-H}
CuA$_2$(CCl$_3$COOH)$_2$	1545(s)	2460-2100	1620(s)	1405(s)	1350(s)
CuB$_2$(CCl$_3$COOH)$_2$	1548(s)	1740(b,s)	1610(s)	1420(s)	1280(b,s) 1290
CuC$_2$(CCl$_3$COOH)$_2$	1550(s)	2440-2100	1615(s)	1405(s)	1358(s)
CuD$_2$(CCl$_3$COOH)$_2$	1547(s)	2460-2200	1625(s)	1412(s)	1358(s)
CuA$_2$(HCCl$_2$COOH)$_2$	1552(s)	2320-2060	1592(s)	1402(s)	1225(s)
CuA$_2$(CF$_3$COOH)$_2$	1548(s)	2420-2260	1625(s)	1415(s)	1218(s)
NiA$_2$(CHCl$_2$COOH)$_2$	1562	1870-1640	1600	1395(sh)	—
NiA$_2$(CCl$_3$COOH)$_2$	1562	1980-1700	1600		1355(sh)
NiA$_2$(CF$_3$COOH)$_2$	1565	1900-1650	1600	1395	1368(sh)
NiB$_2$(CCl$_3$COOH)$_2$	1570	1980-1660	1610	1395(sh)	1365(sh)
NiC$_2$(CCl$_3$COOH)$_2$	1570	2000-1640	1610	1395	1365(sh)
NiC$_2$(C$_6$H$_5$COOH)	1550	1840-1630	1580	—	—
CoA$_2$(CHCl$_2$COOH)$_2$	1565	2180-1650	1595	1390	1365(sh)
CoA$_2$(CCl$_3$COOH)$_2$	1562	2080-1710	1600	1395(sh)	1355
CoA$_2$(CF$_3$COOH)$_2$	1575	1750-1620	1625	1405	—
CoA$_2$(C$_6$H$_5$COOH)	1555	1720-1660	1590	1420(sh)	—
CoB$_2$(CHCl$_2$COOH)$_2$	1665,1595	1980-1630	1612	1400(sh)	—
CoB$_2$(CCl$_3$COOH)$_2$	1570,1580	2100-1690	1610	1392(sh)	1365(sh)
CoB$_2$(CF$_3$COOH)$_2$	1550	1700 (b,s)	1620	1405	1365(sh)
CoC$_2$(CCl$_3$COOH)$_2$	1560	2000-1680	1610	1395	1365

acid, contain two molecules of an acid beside the two hydroxamic acid ligands. In the benzoic acid adducts also, none of the hydroxamic acid ligand is replaced, but they contain only one aromatic acid unlike the corresponding aliphatic acid adducts.

The absorption spectral characteristics of the acid adducts in benzene are found to be the same as those observed when the spectra are recorded with the corresponding nickel(II) and cobalt(II) hydroxamates in the same solvent containing an excess of the acid (Table 2). The positions of the absorption maxima and the low molar extinction coefficients of the acid adducts of nickel(II) and cobalt(II) suggest[10] octahedral stereochemistry. The magnetic moments (Table 3) of these adducts are also compatible with the octahedral structure[11]. The main absorption maxima of the copper(II) adducts in benzene are also normal for octahedral copper(II) complexes having CuO$_6$ chromophore[12,13]. Their magnetic moments (Table 3) also fall in the range expected for octahedral copper(II) complexes without any exchange interaction[14].

In the IR spectra of the hydroxamic acids, the $\nu O-H$ and $\nu C=O$ modes appear at 3060-3120 cm^{-1} and ~1620 cm^{-1} respectively. This lowering of both $\nu O-H$ and $\nu C=O$ is attributed to intramolecular hydrogen bonding[15,16]. On complex formation with metals, the $\nu O-H$ mode disappears and there is a further shift of the $\nu C=O$ towards lower energy (~1500 cm^{-1}). In the acid adducts, the $\nu C=O$ is little affected and consequently appears (Table 4) almost in the same region as found in the original complexes.

New bands, however, appear in the IR spectra of the adducts (Table 4), the most important of which lie above 1600 cm^{-1}.

The appearance of a single asymmetric carboxyl stretch at 1580-1625 cm^{-1} in the acid adducts establishes the coordination of both the carboxylic acid molecules through the carbonyl oxygen. The lowering of carboxyl $\nu O-H$ frequency to such a low value (Table 4) is indicative of the presence of very strong hydrogen bonds[17]. The upward shift of the $\nu O-H$ deformation band also indicates hydrogen bonding. The occurrence of $\nu C=O$ of the hydroxamic acid near 1560 cm^{-1} in the IR spectra of the adducts confirms that the chelating group has not opened up at the $\nu C=O$ end since the $\nu C=O$ is observed in the same region as in the original bis-chelates.

Two different structures may be conceived for the acid adducts based on the above studies. In the first structure (I) it may be assumed that the protons of the carboxyl groups protonate the hydroxamic acid chelates, so that N−O end of the chelate opens up to form N−OH which is then hydrogen bonded to the coordinated carboxylate ion. In this proposition, however, the carboxylate ions will form four-membered chelate rings and the N−OH protons would be hydrogen bonded to the carboxylate oxygens to produce seven-membered intramolecular chelate rings. As pointed out earlier, the IR spectra of free hydroxamic acids show that the N−OH proton is intramolecularly hydrogen bonded to the C=O group of the ligand but $\nu O-H$ is not lowered below 3060
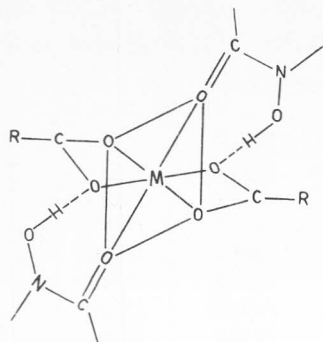
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cm^{-1} by this hydrogen bonding. In the acid adducts the lowering of $\nu O-H$ is very large. Moreover, the strained four-membered carboxylate ring would become more unstable on further hydrogen bonding. Beside these, the separation between the two νCO_2^- modes (200 cm^{-1}) of the carboxyl group is not in favour of the formation of four-membered chelate ring[18].

In the alternate structures (II, III), the original rings of the two hydroxamic acids are not disturbed. The oxygen atoms of the carboxyl group are directly linked to the metal ion and the $O-H$ proton is hydrogen bonded to the $N-O$ oxygen of the chelated hydroxamic acid forming intra- and/or inter-molecular hydrogen bonds resulting in six-membered rings.

The experimentally determined molecular weights (Table 3) of all the six adducts of copper(II) conform to the monomeric structure whereas molecular weight values of some of the more soluble complexes of nickel(II) and cobalt(II) (Table 3) indicate the presence of both monomeric and polymeric forms in benzene solution. Most of these are non-conductors in dry acetonitrile though slight dissociation of some of them cannot be ruled out.

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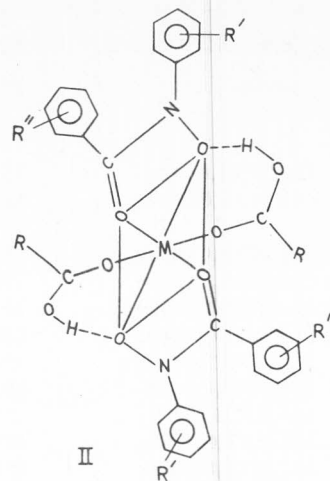
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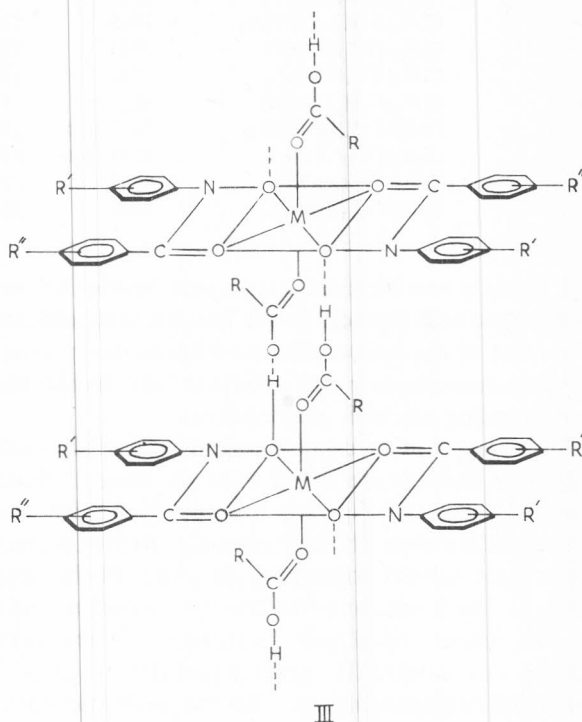
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